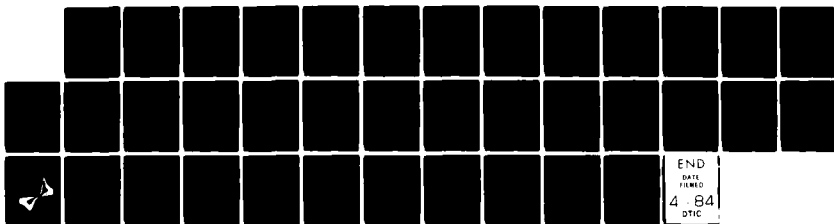


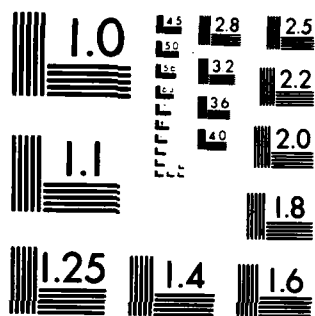
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Chemical Properties and Film Casting of Radiation
Grafted Ion-Containing Polymers

by

Marilyn N. Szentirmay and Charles R. Martin

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College Station, Texas

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Chemical Properties and Film Casting
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Containing Polymers

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Abstract

A series of radiation grafted cation and anion exchange polymers have been studied with the intent of developing procedures for dissolving and film casting these polymers. Solvent swelling studies have shown that these polymers display two maxima in plots of solvent uptake vs. solvent solubility parameter. While similar behavior is shown by the ion exchange polymer Nafion, the anion and cation exchange polymers studied here will not dissolve under conditions (developed by us) which dissolve Nafion. We believe this insolubility results from covalent cross links and/or enhanced crystallinity in the chain material regions of these polymers. These polymers do, however, swell extensively in certain solvents at high temperatures and suspensions may be prepared from the swollen polymer. We have cast films from these suspensions onto electrode surfaces and report initial results of electrochemical characterization of these films.

Introduction

Ion-containing polymer, (ICP) (1,2), membranes have been used as separators in chlor-alkali cells (3) and in cells for energy conversion (4,5), and ICP film-based chemically modified electrodes show promise for use in electrochromics (6), electrocatalysis (7), photo-electrochemistry (8) and electroanalysis (9,10). Further developments in these areas will require ICPs with better mechanical and dynamic properties (11) which can be produced at a lower price (12). Accordingly, this research group has been investigating the fundamental chemical and electrochemical properties of a variety of ICPs (13,14) and studying possible new applications for these polymers (10,15).

We report at this time results of studies of ICPs prepared by derivitizing, through radiation grafting, polyethylene (PE) and polytetrafluoroethylene (PFE) sheets (12,16). Both cation exchange polymers (sulfonated PEs and PFEs) and anion exchange polymers (quaternized PEs and PFEs) were studied. These polymers are of interest because they may prove to have the desirable chemical and transport properties of Nafion, a highly successful perfluorosulfonate polymer (1,13,14), but can be produced at lower costs (12). The quaternized polymers are of particular interest to us because they may prove to be cationic versions of Nafion and thus be useful when anion exchange or transport is needed.

The purposes of the work described here were to use solvent swelling studies (12,17) to develop procedures for film casting these radiation grafted ICPs and to use electrochemical methods for preliminary investigations of the physical and transport properties of the resulting films. Particular emphasis is placed on the quaternized polyethylene polymer.

Experimental

Materials. The ICPs and polyethylene were obtained from RAI Research Corporation (Hauppauge, NY). The sulfonated polyethylene (PE-SS, 700 g/mole $\text{-SO}_3\text{H}$) and the sulfonated polytetrafluoroethylene (PFE-SS, 850 g/mole $\text{-SO}_3\text{H}$) are prepared by grafting styrene onto sheets of the polymer, followed by sulfonation of the styrene (12,16). The quaternized polyethylene (PE-QA, 1100 g/mole N) and the quaternized polytetrafluoroethylene (PFE-QA, 1000 g/mole N) are prepared by grafting vinylbenzylchloride onto the polymers and quaternized with triethylamine (16). Membranes were converted to various counterionic forms by soaking in appropriate salt or acid solution.

Water was triply distilled or obtained from a Milli-Q water purification system (Millipore Corp., Bedford, MA). 2-Ethylhexanol, 1-decanol, 2-ethylbutanol, 1-pentanol, ethylene glycol, sodium anthraquinone-2-sulfonate, disodium anthraquinone-2,6-disulfonate, and sodium hexafluorophosphate were obtained from Aldrich Chemical Co. (Milwaukee, WI). Xylene was obtained from Center Chemical Co. (Austin, TX). Triethylamine was obtained from MCB (Cincinnati, OH). Hydroquinone was obtained from J. T. Baker Chemical Co. (Phillipsburg, NJ). Trifluoroacetic acid (TFA) was obtained from Sigma Chemical Co. (St. Louis, MO). $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$ was obtained from Johnson Matthey, Inc. (Winslow, NJ). 8-Hydroxy-1,3,6-pyrenetrisulfonic acid, trisodium salt was obtained from Eastman Kodak Co. (Rochester, NY) and recrystallized twice from aqueous acetone. $\text{Ru}(\text{bpy})_3\text{Cl}_2$ (bpy = 2,2'-bipyridine) was obtained from G. F. Smith. All other chemicals were reagent grade.

Solvent Swelling Measurements. Studies similar to those described by Yeo, et al. (12,17) were done. The membranes (0.06-0.10 g) were immersed in the

desired solvent in a capped vial at room temperature for at least two days, then removed, blotted dry, and weighed immediately in a closed weighing bottle. The membranes were then replaced in the solvents and re-weighed more than one day later to insure that no further solvent uptake had occurred. Each value of % increase in weight is the average of two or more experiments. In almost all cases, reproducibility was better than $\pm 5\%$.

Preparation of Polymer Suspensions. Specific conditions used to soften the ion exchange polymers are given in the Results and Discussion section. The pressure reactor (Parr Instrument Co., Moline, IL) was purged with N_2 before sealing. In some cases, N_2 was added after sealing to increase the pressure in the reactor. The contents of the reactor were stirred while heating. Prior to heating in the reactor, PFE-SS was ultrasonically cleaned in 50:50 ethanol-water to remove a pink color. The softened polymers were ground in a glass tissue grinder driven by an overhead stirring motor. Titrations to check the manufacturers listed value of the ion exchange capacity of PE-QA (chloride form) were done by equilibrating a known weight of polymer with aqueous KNO_3 and titrating the Cl^- released with $AgNO_3$. Chlorofluorescein was used as the indicator.

Preparation of Electrode Films. Glassy carbon (1/8 in. diameter, Atomergic Chemetals Corp., Plainview, NY) was polished as described previously (14). Films of PE-SS and PE-QA were cast onto glassy carbon electrodes from suspensions in propanol, PFE-QA from a suspension in 50:50 ethanol-water, and PFE-SS from a suspension in 50:50 ethylene glycol-ethanol. The electrodes were coated by syringing a measured amount of polymer suspension onto the electrode surface (14). After the solvent evaporated (in air), the polymer-coated electrodes were soaked at least 6 hr in supporting electrolyte before use. This served to both hydrate the film and wash out any residual solvent. Wet film thicknesses were measured with an Alpha-step surface

profiler (Tencor Instruments, Mountain View, CA).

Electrochemical measurements. A PAR Model 174 potentiostat and Model 175 programmer (EG & G PAR, Princeton, NJ), an X-Y recorder (Houston Instruments, Austin, TX) and a Nicolet 2090-3 digital oscilloscope (Nicolet Instrument Corp., Madison, WI) were used for electrochemical experiments. A three-electrode cell with a saturated calomel reference electrode (SCE) and a Pt disk counter electrode was employed. All electrochemical measurements were done in N_2 -degassed solutions.

Results and Discussion

Solvent Swelling Studies. Yeo, et al. (12,17) have found that Nafion and the sulfonated RAI membranes exhibit two maxima in plots of solvent uptake vs. solvent solubility parameter. We have shown that Nafion may be dissolved at high temperatures in binary solvent systems composed of a solvent which has a solubility parameter near the first swelling maximum and a solvent which has a solubility parameter near the second swelling maximum (13). It was of interest to us to see if a similar approach could be used to dissolve the various RAI membranes. If so, chemically modified electrodes based on films of these polymers could be prepared. Such electrodes allow for convenient evaluation of the charge transport properties (14) and the ion exchange thermodynamics (10) of ICPs.

Solvent swelling studies are also of interest because they can be used to deduce information about ICP morphology (vide infra). Solvent swelling data are already available for the sulfonated RAI polymers (12). We report results of swelling studies of PE-QA. Since the solvents used varied in hydrogen bonding ability, three component solubility parameters (δ) (18,19) were used for these studies. The solvents and their solubility parameters are listed in Table I.

Results of the solvent swelling studies of PE-QA are shown in Figures 1-3. In pure solvents, the Cl^- form of PE-QA exhibits two swelling maxima, one at approximately 10 Hb, the other a broad maximum in the range 15-20 Hb (Figure 1). As noted above, similar results were obtained with Nafion (17), PFE-SS and PE-SS (12). In propanol-water mixtures, PE-QA chloride exhibits solvent uptakes greater than those observed in either pure propanol or pure water (Figure 2). Again, this type of behavior was also observed with Nafion (17). Finally, when PE-QA is converted from the Cl^- form to the PF_6^- form its solvent swelling characteristics change dramatically (Figure 3). While nearly all of the solvents swell the PF_6^- form much less extensively, it is of particular interest to note that the low δ envelope is essentially completely wiped out.

It is now fairly well established that many ICPs are, on a microscopic level, biphasic (20). Yeo, et al. (12,17) have concluded that in Nafion, PFE-SS and PE-SS, the high solubility parameter envelope results from interactions in the ionic cluster phase (20) and the low solubility parameter envelope results from interactions with the organic chain material phase or with the sidechains. The fact that two δ maxima are observed in PE-QA Cl^- suggests that this ICP is also biphasic. Because polyethylene (the chain material in PE-QA) has a δ of about 8 (21) and the first swelling maxima occurs at $\delta = 10$, it is reasonable to conclude that the low δ maximum in PE-QA results primarily from interactions with the sidechains. A comparison of solvent uptake data for PE-QA with data for the polyethylene used by RAI to make PE-QA (Table II) supports this conclusion. The solvents which produce the greatest swelling in PE-QA do not appreciably swell polyethylene.

That the low δ maximum is attributable to interactions with the sidechains is also supported by the PF_6^- swelling data. It is generally

accepted that counterions are localized in the ionic domains of ICPs and not in the surrounding chain material phase (20). Therefore, if the swelling maximum at 10 Hb were due primarily to interactions with the chain material, the tremendous sensitivity of swelling to the nature of the counterion would not be expected. Furthermore, by the same argument, since the sidechain interactions are very sensitive to counterion, it seems likely that the sidechains intrude into the ionic domains. This intrusion of organic sidechain explains why luminescence probe studies of these ICPs indicate that the cluster phase is rather hydrophobic (22,23).

Polymer Suspensions. The swelling studies revealed several solvents and solvent systems which showed promise for dissolving PE-QA chloride (e.g., 50:50 ethanol water and dimethylsulfoxide). However, PE-QA would not dissolve in any solvent or solvent system, even at high temperatures and pressures. The failure of PE-QA to dissolve is surprising, since a similar approach was successfully used to dissolve Nafion (13). Since cluster formation may be regarded as electrostatic cross-linking (24), it seemed possible that the clusters might be responsible for the insolubility. To test this possibility, PE-QA chloride membranes were immersed for several hours in boiling xylene. This caused the charged sites to cleave from the membrane.* The uncharged membranes were then boiled in fresh xylene for several more hours. While boiling xylene will dissolve the polyethylene used to prepare PE-QA, it did not dissolve the decharged PE-QA. This shows that the presence of the charged groups (and, therefore, cluster formation) is not responsible for the insolubility. We believe that covalent cross-

*When as-received membranes are immersed in an aqueous solution of the fluorescent anion 8-hydroxy-1,3,6-pyrenetrisulfonate, strong fluorescence from the cationic membrane is observed. After treatment in boiling xylene, and reimmersion in the fluorophore solution, no fluorescence can be detected from the membrane.

links are introduced during the radiating grafting procedure; even a minute amount of cross-linking would render this polymer insoluble in any solvent.

We were also unable to dissolve PE-SS, PFE-QA and PFE-SS. PE-SS is probably also covalently cross-linked but tetrafluoroethylene polymers show little tendency to cross-link when bombarded with radiation (16). The insolubility of these polymers in solvent systems which will dissolve Nafion may result from higher degree of crystallinity in the starting PFEs than in Nafion. The Nafions which we successfully dissolved (13) by heating to 250°C have melting points around 210°C (25). The melting point of the polytetrafluoroethylenes are around 350°C (26). While in principle this indicates that PFE-QA and PFE-SS could be dissolved at higher temperatures, we have found that in the solvents studied here the charged sites begin to cleave from PFE-QA at temperatures above about 150°C and from PFE-SS at temperatures above about 300°C.

In spite of their insolubility, we were able to cast films of all of these ICPs. This was accomplished by using the solvent swelling experiments to identify strongly swelling solvents, using these solvents in the high temperature reactor to soften the polymers, and then grinding the wet, softened polymer in a ground glass tissue grinder. Suspensions of the polymers resulted; these suspensions were filtered to remove the larger particles and then used to cast films. The conditions required to soften each polymer are shown in Table III. As noted above, temperatures high enough to soften PFE-QA also cleaved the charged sites. For this reason, we were forced to use lower than optimal temperatures, and poor softening resulted.

A comparison of the ion exchange capacities of PE-QA chloride before treatment and after suspension showed that charged sites are not destroyed during the softening and grinding process. The ion exchange capacities were 0.95 meq./g for the as-received membranes and 0.94 meq./g after suspension.

Polymer-Coated Electrodes. Films cast from the ICP suspensions were examined with a surface profilometer. These studies showed that, while the entire electrode surface was covered, the coatings were uneven, as might be expected for films composed of small adhering particles. Thickness measurements on wet PE-QA films gave densities of 0.69 g/cm^3 ; the density of the dry, as-received membrane is 0.65 g/cm^3 (27). Figure 4A shows background currents observed at a bare glassy carbon electrode. Figures 4B through E show analogous background currents for electrodes coated with the various RAI polymers. As would be expected (13), background currents do not change appreciably after coating.

As has been observed with other ICP-based chemically modified electrodes (13,28,29), the RAI films incorporate and retain electroactive counterions and allow for charge transport to and from these ions. For example, Figure 5A shows a series of cyclic voltammograms recorded after a PE-QA coated electrode was immersed in a solution of anthraquinone sulfonate (AQS). Current increased with time, eventually reaching a steady state level (13,28,29). When the electrode was removed from solution, rinsed, and placed in supporting electrolyte, current due to the retained AQS was observed. Voltammogram 5B was recorded 35 min after the coated electrode was placed in supporting electrolyte. While when immersed in supporting electrolyte, AQS is slowly leached from the polymer, the film itself remained attached to the electrode and could be reloaded with AQS to

the same voltammetric current level shown in the last scan in Figure 5A. Analogous results were obtained with the other RAI polymers.

Preliminary investigations of the charge and mass transport properties of PE-QA films at electrode surfaces were also carried out. Figure 6A shows that voltammetric peak currents, i_p , for polymer-bound AQS are proportional to the square root of scan rate. This is the expected (28) dependency in the thick (ca. 4 μM) films used here. Potential step chronocoulometry for AQS and anthraquinone-2,6-disulfonate (AQDS) in PE-QA films produced linear charge vs. $t^{1/2}$ plots (Figure 6B). Apparent diffusion coefficients (14,28) of about $1 \times 10^{-9} \text{ cm}^2/\text{s}$ were obtained, from such plots, for both the oxidized and reduced forms of AQS and AQDS.

Figures 5 and 6 show that PE-QA extracts and transports electroactive counterions. It was also of interest to evaluate the extent to which neutrals and coions permeate the film. We have found that small, neutral molecules (e.g., hydroquinone) readily penetrate films of PE-QA; in fact, peak currents for hydroquinone at coated electrodes are identical to those at uncoated electrodes. These molecules are not, however, retained by the film in that no trace of the hydroquinone voltammetric wave is observed when a PE-QA modified electrode is transferred from a hydroquinone solution to a solution containing only supporting electrolyte.

Coions (e.g., $\text{Ru}(\text{bpy})_3^{2+}$, $\text{Ru}(\text{NH}_3)_6^{3+}$) also penetrate PE-QA films. Peak currents for these ions are, however, reduced to less than about 25% of the peak currents observed for the same solution at an uncoated electrode. Coions are also not retained by these films. The ability of coions to penetrate the rather thick (4 μM) films used here suggests that there are pinholes or channels through the films. Again this is not surprising given the fact that these films are composed of adhering particles. We are

currently investigating the possibility of using annealing procedures to reduce the void volumes of these films.

Conclusions

Solvent swelling studies have provided a method for film casting the RAI ICPs. While these polymers show solvent swelling characteristics very similar to Nafion, they will not dissolve in solvents which dissolve Nafion (e.g., 50:50 ethanol-water (13), dimethylsulfoxide (29), propylene carbonate (30)). We suggest that cross-linking introduced during the grafting procedure or enhanced crystallinity cause this lack of solubility. The solvent swelling studies have also provided information about the polymer-solvent interactions which produce swelling and about the morphology of PE-QA. More importantly, these studies have shown that the chemical properties of the PE-QA ionomer are strongly dependent on the nature of the counterion.

Because of the ability to cast films, charge transport properties and ion exchange thermodynamics of these polymers may now be conveniently evaluated. In previous studies, we have shown that Nafion preferentially binds hydrophobic counterions (10,15,28) and that hydrophobic interactions can influence rates of diffusion in Nafion films at electrode surfaces (14). It will be of interest to see if hydrophobic interactions are of importance to ion exchange and charge transport in films of the RAI polymers.

Acknowledgements

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Table 1

Solvents and Solubility Parameters

Solvent	Solubility Parameter ^a (cal cm ⁻³) ^{1/2} , Hb
Triethylamine	7.4 ^b
Heptane	7.5 ^c
4-Methyl-2-pentanone	8.6
Xylene	8.8
2-Ethylhexanol	9.8
1-Decanol	10.0 ^c
2-Ethylbutanol	10.4
1-Pentanol	10.6
1-Butanol	11.3
1-Propanol	12.0
N,N-Dimethylformamide	12.1
Dimethylsulfoxide	12.9
Ethylene glycol	16.3
Formamide	17.8
Glycerol	21.1
Water	23.5

^aall values from reference (19), except as noted.

^bvalue from reference (21).

^cvalue calculated from reference (18).

Table 2

Solvent Uptake Measurements for Polyethylene and PE-QA

Solvent	% Increase in Weight Polyethylene	PE-QA
Xylene	13	17
Decanol	2	60
Butanol	<1	42
DMSO	0	52
H ₂ O	0	42

Table 3

Summary of Conditions Used to Suspend RAI Polymers

Polymer	Counterion	Solvent	Temperature (°C)	Pressure (psi)	Time (hr)
PE-QA	Cl ⁻	50:50 Propanol-Water	150	100	4
PE-SS	Li ⁺	Methanol	150	250	4
PFE-SS	Li ⁺	Ethylene Glycol	250	730	3
PFE-QA ^a	OH ⁻	50:50 Propanol-Water	150	100	4

^avery little softening.

Figure Captions

Figure 1. Solvent uptake vs. solubility parameters of solvents for PE-QA, chloride form.

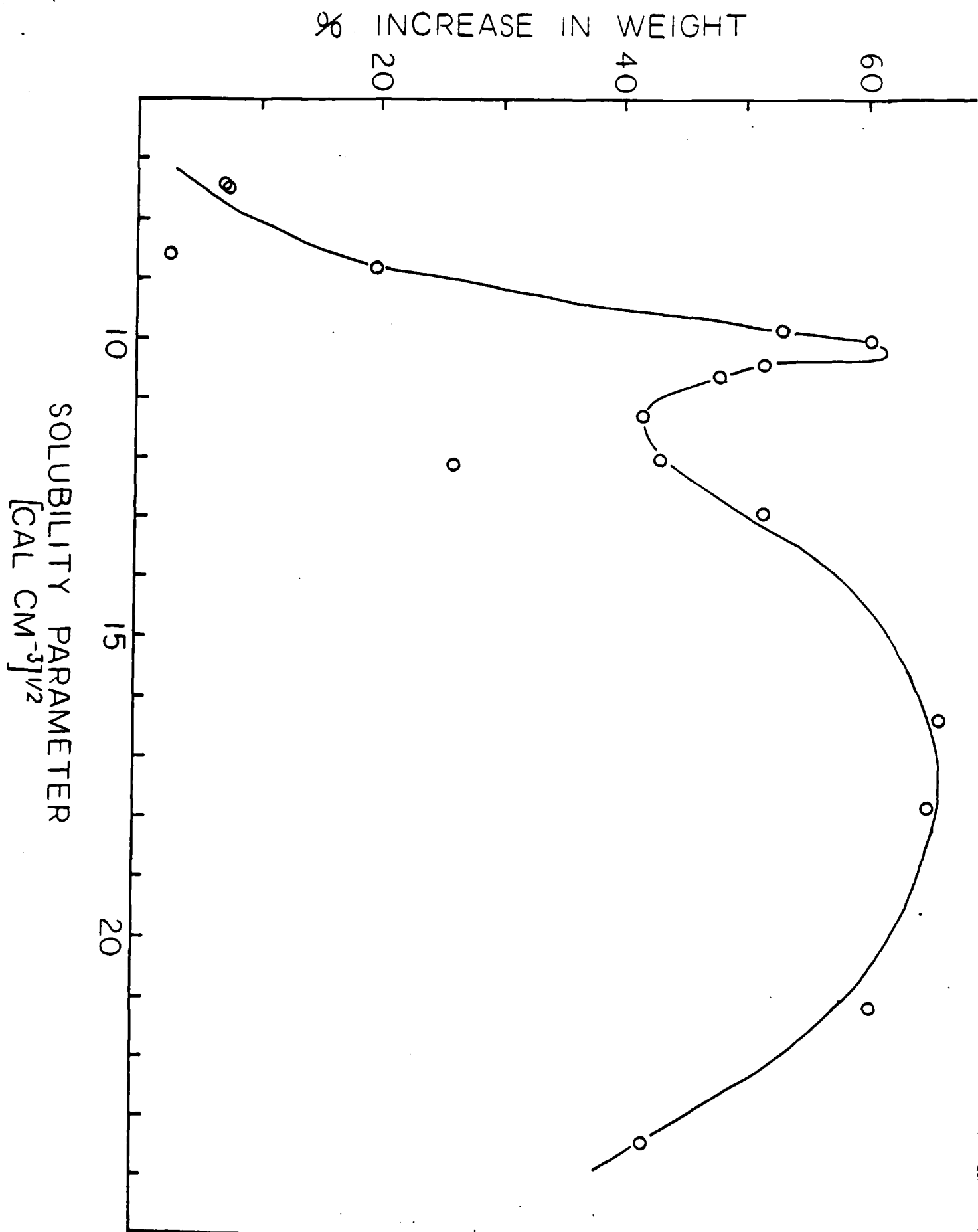
Figure 2. Solvent uptake of PE-QA, chloride form vs. solubility parameters, δ_{Mix} , propanol-water mixtures. $\delta_{\text{Mix}} = V_{\text{PrOH}} \delta_{\text{PrOH}} + V_{\text{H}_2\text{O}} \delta_{\text{H}_2\text{O}}$ (17), where V_{PrOH} and $V_{\text{H}_2\text{O}}$ are volume fractions, and δ_{PrOH} and $\delta_{\text{H}_2\text{O}}$ are solubility parameters, of propanol and water.

Figure 3. Solvent uptake vs. solubility parameters of solvents for PE-QA, PF_6^- form.

Figure 4. Cyclic voltammetric background currents recorded at 0.1 v/s. A. Uncoated glassy carbon electrode in 0.2 M NaTFA, pH 3.0. B.-E. Glassy carbon electrodes coated with: B. PFE-SS, $\sim 10^{-7}$ moles $\text{SO}_3^-/\text{cm}^2$ (0.2 M NaTFA, pH 3.0). C. PE-SS, 4.5×10^{-7} moles $\text{SO}_3^-/\text{cm}^2$ (0.2 M NaTFA, pH 3.0). D. PFE-QA, 6.3×10^{-7} moles quaternary ammonium sites/ cm^2 (0.1 M TFA/0.1 M NaTFA). E. PE-QA, 2.4×10^{-7} moles quaternary ammonium sites/ cm^2 (0.1 M TFA/0.1 M NaTFA).

Figure 5. Cyclic voltammograms of AQS recorded at a scan rate of 0.1 v/s. Supporting electrolyte = 0.2 M NaTFA, pH 3.0. A. Loading of PE-QA film (4.5×10^{-7} moles quaternary ammonium sites/ cm^2 , 7 μm thick) from 2.3×10^{-4} M AQS. First scan recorded immediately after immersion. Last scan recorded 1 hr 35 min later. B. Same PE-QA film after loading, rinsing and soaking in supporting electrolyte for 35 min. C. Steady state voltammogram of 2.3×10^{-4} M AQS on bare glassy carbon electrode.

Figure 6. A. Anodic peak current, i_p , vs. square root of scan rate, $v^{1/2}$, for AQS in a PE-QA film (2.4×10^{-7} moles quaternary ammonium sites/cm², 4 μ m thick). Supporting electrolyte: 0.1 M TFA/0.1 M NaTFA. B. Chronocoulometric plot of charge (Q) vs. $t^{1/2}$ for reduction of AQS in PE-QA electrode described in Figure 4D. Supporting electrolyte: 0.2 M NaTFA, pH 3.0.



% INCREASE IN WEIGHT

20

40

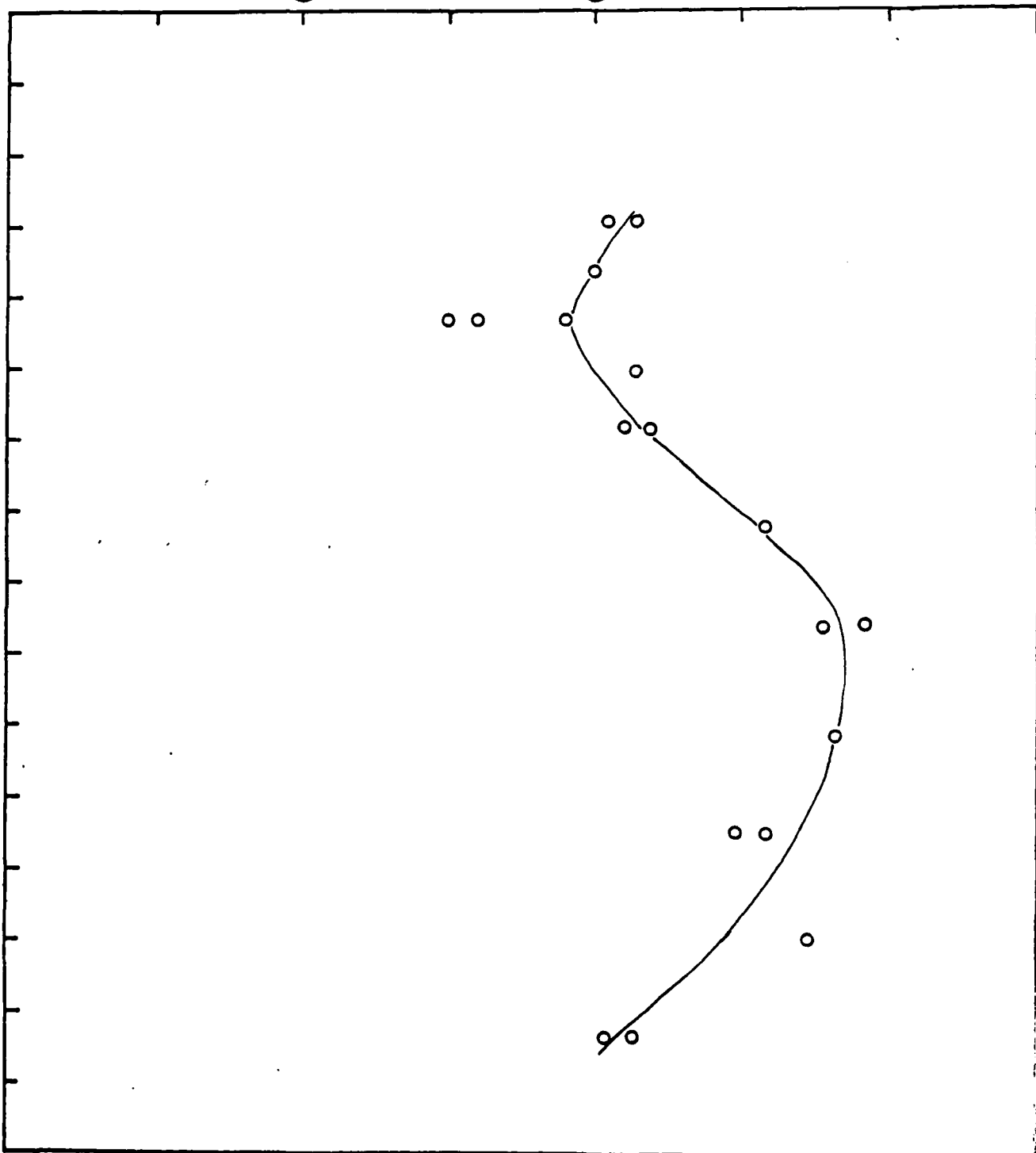
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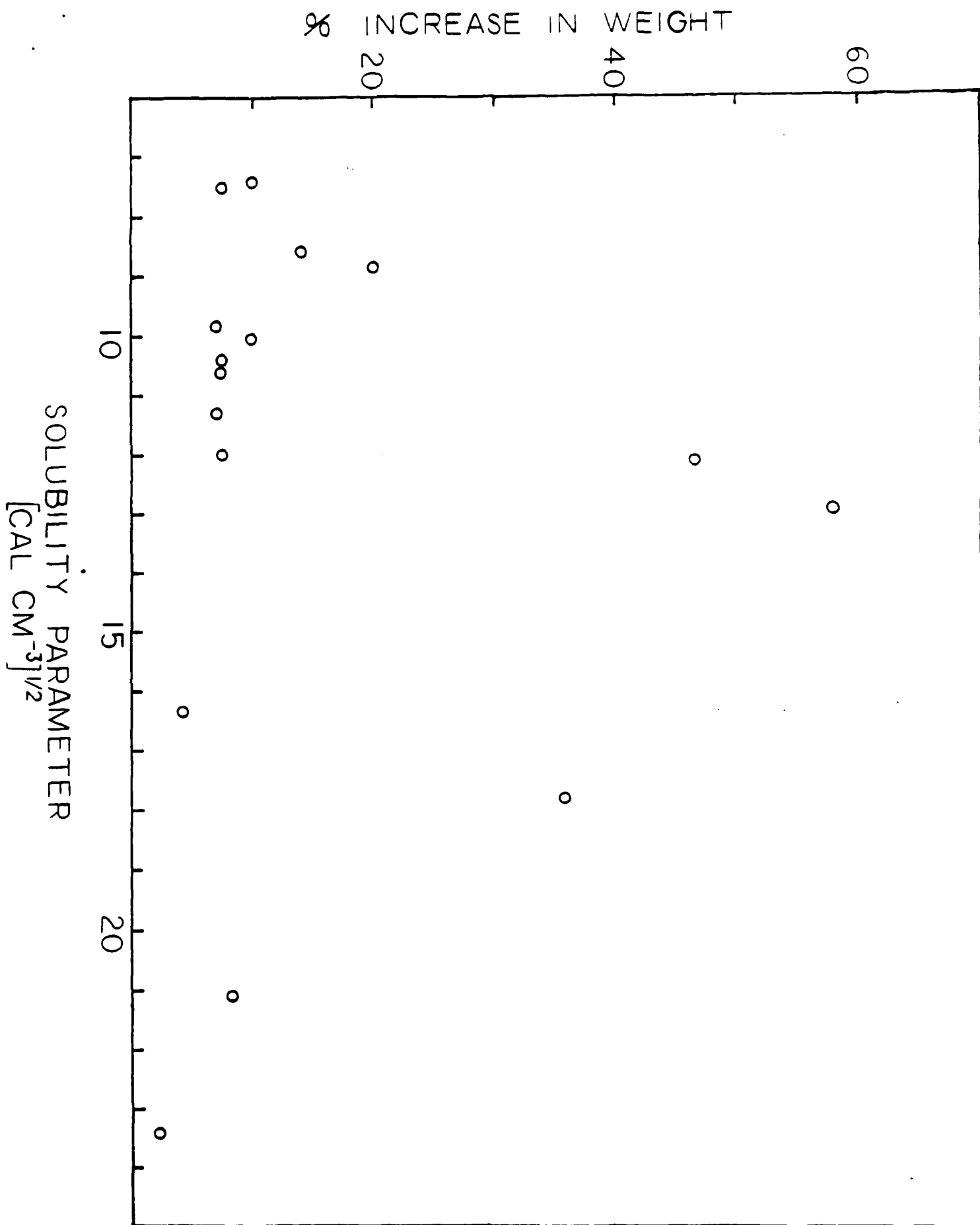
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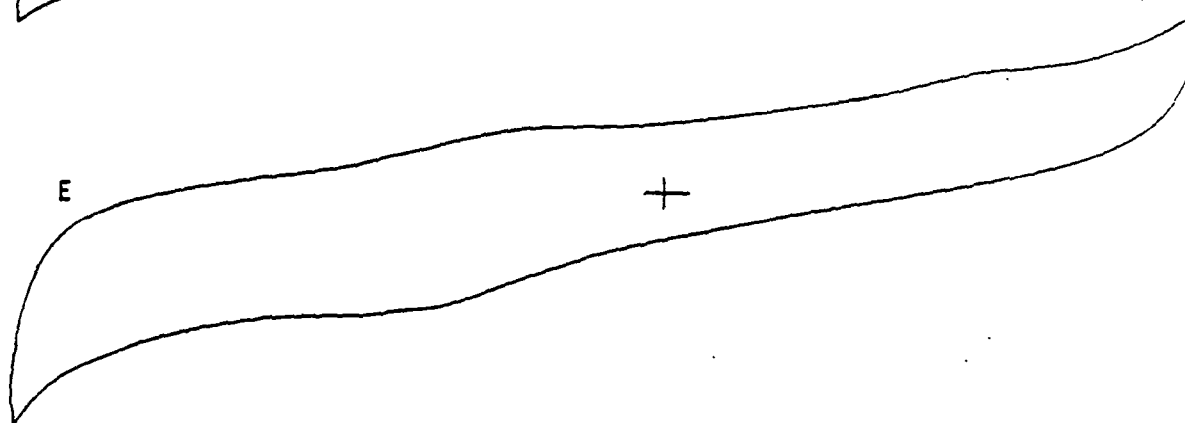
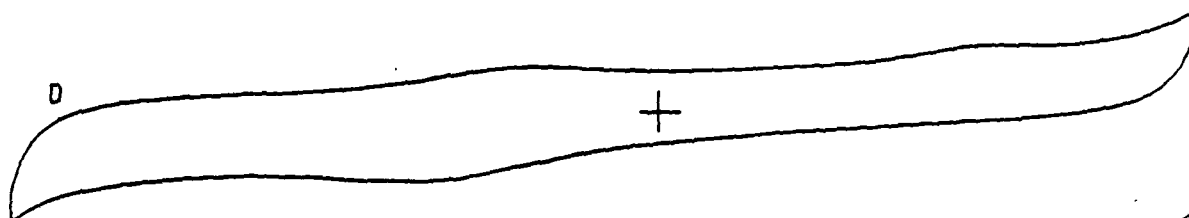
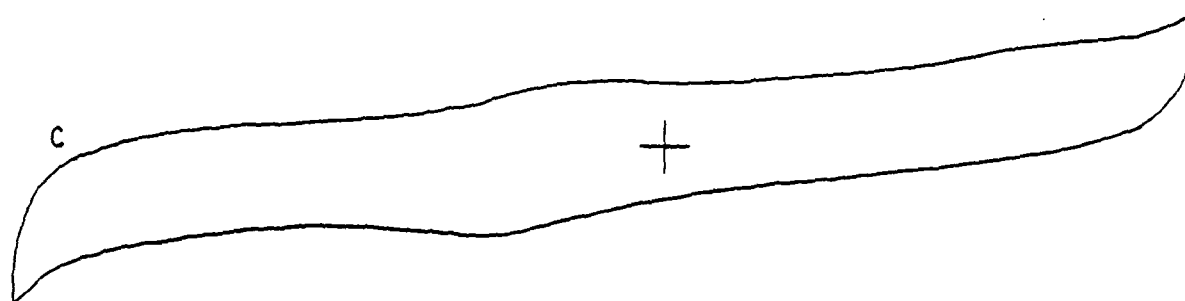
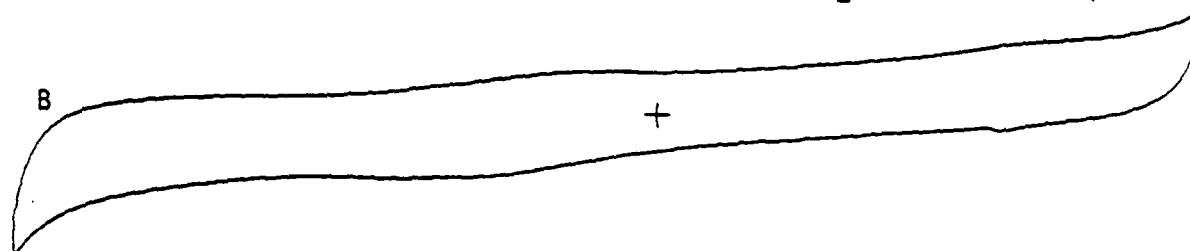
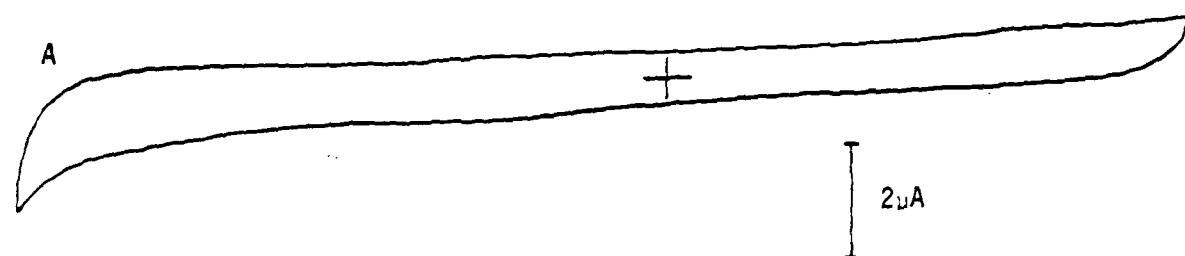
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SOLUBILITY PARAMETER
 $[\text{CAL CM}^{-3}]^{1/2}$



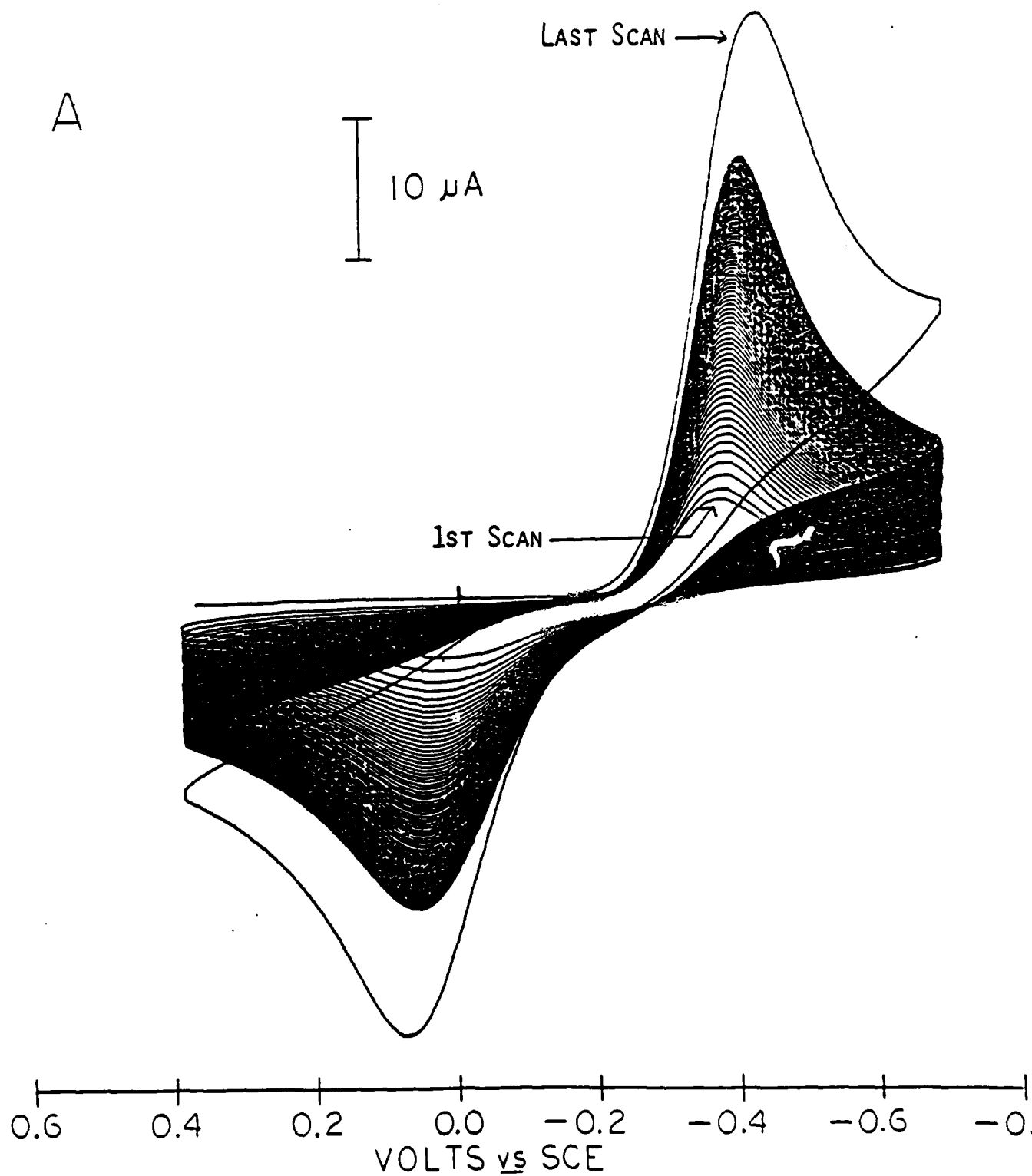




1.2 1.0 0.8 0.6 0.4 0.2 0.0 -0.2 -0.4 -0.6 -0.8 -1.0

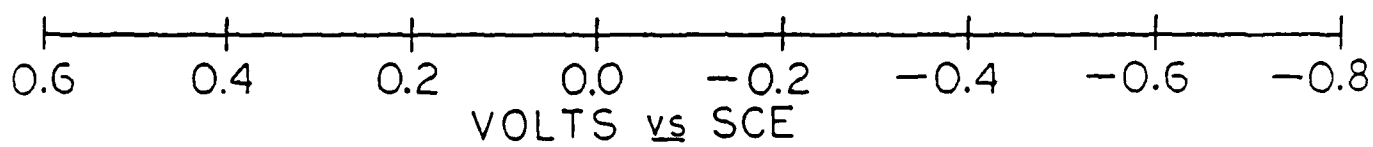
VOLTS vs SCE

A



B

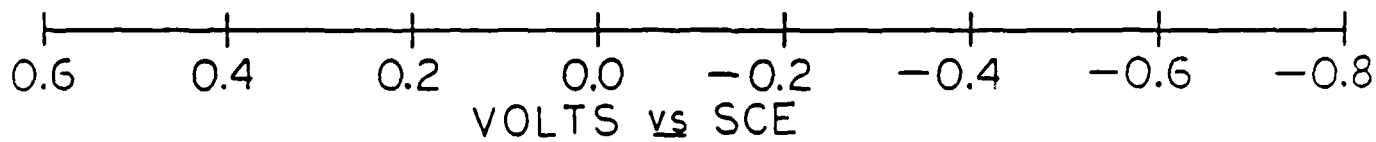
10 μ A

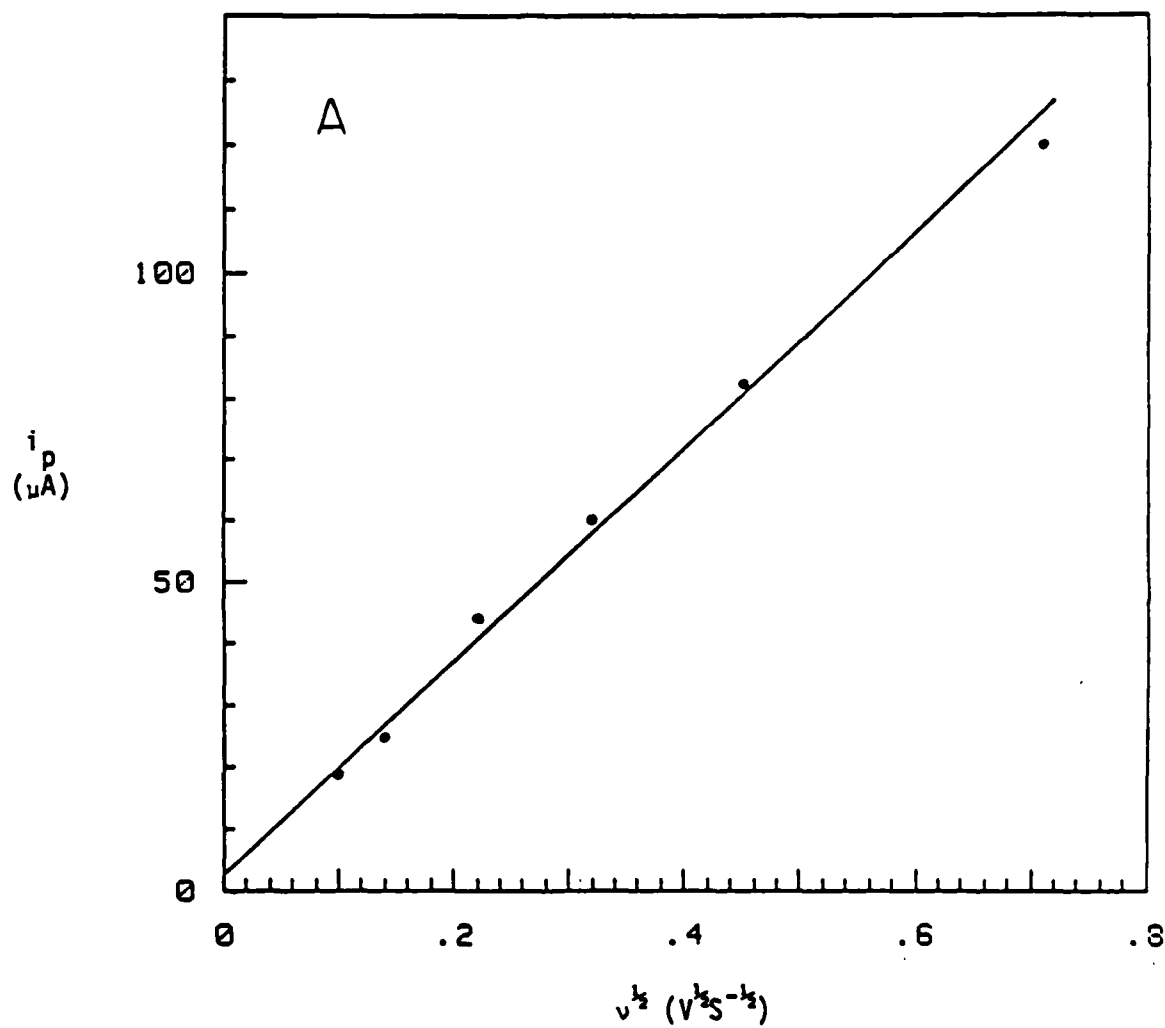


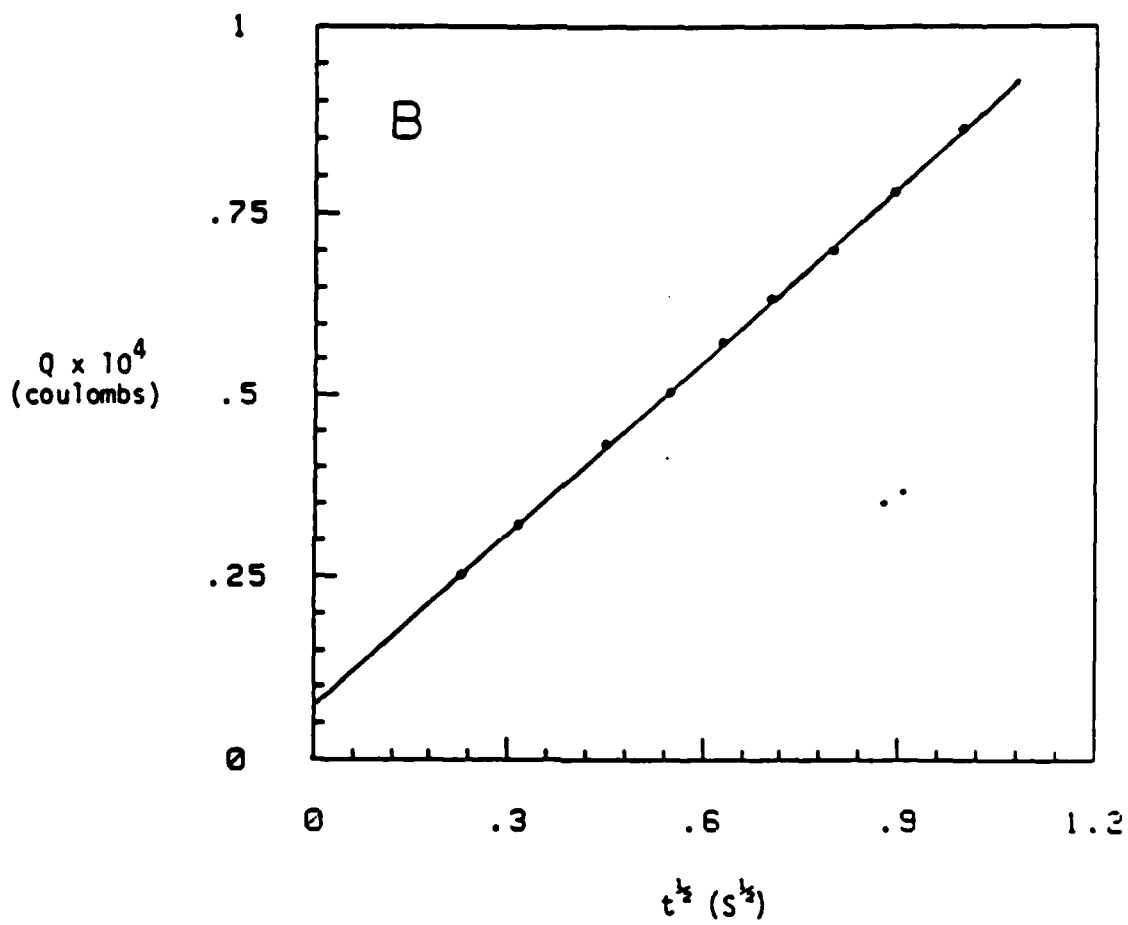
C



10 μ A







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